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Translation of

Japanese Laid-open (Kokai) Patent Application HEI 2-91980 (A)

Application No.: Sho 63-244806
Application date: September 29, 1988
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Applicant: TOSHIBA LITECH K.K. [Toshiba Lighting & Technol. Corp.]

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1. Title of the invention

Solid-state light emitting element

2. What is claimed is:

(1) A solid-state light emitting element, characterized by comprising a substrate made up of a p-type boron nitride crystal layer including a minute amount of Be, and an n-type boron nitride crystal layer formed on the said crystal layer and including a minute amount of Si; a layer of particulate phosphor with a particle size of 0.3 - 13 μm which covers at least the junction interface of said p-type and n-type boron nitride crystal layers on the side portions of said substrate; and electrodes respectively formed on an upper surface and a lower surface of said substrate.

(2) A solid-state light emitting element, characterized by comprising a substrate made up of a p-type boron nitride crystal layer including a minute amount of Be, and an n-type boron nitride crystal layer formed on the said crystal layer and including a minute amount of Si; a thin-film phosphor layer with a film thickness of 0.6 - 2.6 μm which covers at least the junction interface of said p-type and n-type boron nitride crystal layers on the side portions of said substrate, and electrodes respectively formed on an upper surface and a lower surface of said substrate.

3. Detailed description of the invention

Object of the invention

Field of industrial application

The present invention relates to an improvement to solid-state light emitting elements having a pn junction interface.

Prior art

As a result of technological advances in electronics over the recent years, not only discharge tubes are used any more as light-emitting elements, but solid-state light emitting elements are finding an increasingly wide use.

As a prior art representative for solid-state light emitting elements there is known, for example, a red light emitting element as shown in Fig. 2 and having the following structure: on an n-type GaP crystal substrate 1, an n-type GaP epitaxial layer 2 including a minute amount of Te and a p-type GaP epitaxial layer 3 including a minute amount of Zn and O are formed; furthermore electrodes 4, 5 are respectively formed on this p-type GaP epitaxial layer 3 and on the rear surface of the substrate 1. Apart from this, though not pictorially represented, there are also known red light emitting elements using a pn junction of GaAsP and GaAlAs on an n-type GaAs substrate; orange and yellow light emitting elements using a pn junction of $GaAs_{1-X}P_X$ on the said substrate; green light emitting elements using a pn junction of GaP on the said GaP; blue light emitting elements using a pn junction of SiC on SiC.

Despite their advantages of a small size and good consistency with electronic circuitry, these solid-state light emitting elements were nevertheless limited to the emission wavelengths that are characteristic for the respective types of light-emitting elements; even if light emission of another color were to be selected, the very types of solid-state light emitting elements are few, and light emission having a desired color was difficult to achieve.

Problems to be solved by the invention

The present invention was conceived before the background of this situation with the purpose of furnishing a solid-state light emitting element providing various colors of emitted light while having the same kind of pn junction.

Constitution of the invention

Measures for achieving the object

The first invention of the present application is a solid-state light emitting element which is characterized by comprising a substrate made up of a p-type boron nitride crystal layer including a minute amount of Be, and an n-type boron nitride crystal layer formed on the said crystal layer and including a minute amount of Si; a layer of particulate phosphor with a particle size of 0.3 - 13 μm which covers at least the

junction interface of the p-type and n-type boron nitride crystal layers on the side portions of the substrate; and electrodes respectively formed on an upper surface and a lower surface of the substrate.

The second invention of the present application is a solid-state light emitting element which is characterized by comprising a substrate made up of a p-type boron nitride crystal layer including a minute amount of Be, and an n-type boron nitride crystal layer formed on the said crystal layer and including a minute amount of Si; a thin-film phosphor layer with a film thickness of 0.6 - 2.6 μm which covers at least the junction interface of the p-type and n-type boron nitride crystal layers on the side portions of the substrate, and electrodes respectively formed on an upper surface and a lower surface of the substrate.

In the first invention of the present application, when the size of the particles of which the layer of particulate phosphor is composed, is outside the range of grain sizes between 0.3 and 13 μm, it is not possible to achieve a sufficient emission intensity. Also in the second invention of the present application, when the film thickness of the phosphor layer is outside the range of 0.6 to 2.6 μm, it is not possible to achieve a sufficient emission intensity.

When the present inventors applied a forward-biased current of, e.g., 0.5 mA prior to forming the said phosphor layer, a light emission spectrum having a peak wavelength in the 200 - 400 nm ultraviolet range in accordance with the representation in Fig. 3 was mainly achieved. Thereupon the inventors experimented with forming various phosphor layers having different particle sizes and film thicknesses on the pn junction, whereby they managed to arrive at the above described invention(s).

In the following, the present invention shall be explained in more detail by referring to Fig. 1.

In the figure, 11 denotes a p-type boron nitride crystal layer including a minute amount of Be (hereinafter: p-type layer). On this p-type layer 11, an n-type boron nitride crystal layer 12 including a minute amount of Si (hereinafter: n-type layer) is formed. For the present purposes, this p-type layer 11 and n-type layer 12 shall jointly be referred to as the substrate.On the side walls of this substrate, a particulate phosphor layer 13 comprised of particles having particle sizes of 0.3 - 13 μm is formed. There is no need to form this phosphor layer 13 so as to extend over the entire side wall, but it is

sufficient if it at least covers the junction portion of p-type layer 11 and n-type layer 12. Electrodes 14, 15 are respectively formed on the upper and lower surfaces of the substrate.

Function

Through the formation of various phosphor layers of different particle sizes and film thicknesses, the present invention makes it possible to obtain solid-state light emitting elements with the same kind of pn junction that provide various colors of emitted light.

First embodiment

A self-activating phosphor $MgWO_4$ was mixed into a solution of 6% (wt.) of nictrocellulose, 2.5% (wt.) of ethanol, 86.5% (wt.) of butyl acetate, 5.0% (wt.) of diethyl phthalate by stirring. Then a solid-state light emitting element was obtained by applying these $MgWO_4$ particles on the substrate side walls including the above mentioned pn junction portion, heating to 400°C, and then cooling to room temperature so as to form the phosphor layer.

When a forward-biased current of 2 mA having a voltage of 20 V was applied between the electrodes of the solid-state light emitting element obtained in this way, a light emission spectrum having a peak wavelength at 480 nm was obtained which exhibited a blue light emission. Furthermore phosphor layers of $MgWO_4$ powder of various particle sizes were respectively formed on the pn junction portions by the same method as set forth above, the light emission spectrum was measured, the relative emission intensities at the peak wavelength of 480 nm were determined, and the relationship between relative emission intensity and phosphor particle size as shown in Fig. 4 was determined. In accordance with this figure, when the phosphor particle size was 0.6 μm or less, the luminous efficiency of the phosphor was extremely poor and was reduced to less than 20% in comparison with a phosphor particle size of about 4.0 μm at which a maximum emission intensity was obtained, and there was hardly any contribution to light emission. With phosphor particle sizes of 11 μm and more, on the other hand, the relative emission intensity was equally reduced to less than 20%, so that the contribution to light emission was small. In accordance with the above, a particle size of 0.6 - 11 μm is preferred for the $MgWO_4$ making up the phosphor layer.

Second embodiment

A self-activating phosphor $CaWO_4$ as the test powder was dispersed in an organic solution in the same way as in the first embodiment and mixed by stirring. Then a solid-state light emitting element was obtained by applying these $MgWO_4$ particles on the substrate side walls including the above mentioned pn junction portion, heating to 470°C, and then cooling to room temperature so as to form the phosphor layer.

When a forward-biased current of 3 mA having a voltage of 30 V was applied between the electrodes of the solid-state light emitting element obtained in this way, a light emission spectrum having a peak wavelength at about 415 nm was obtained which exhibited a blue light emission.

Furthermore phosphor layers of $CaWO_4$ powder of various particle sizes were respectively formed on the pn junction portion by the same method as set forth above, the light emission spectrum was measured, the relative emission intensities at the peak wavelength of 480 nm were determined, and the relationship between relative emission intensity and phosphor particle size as shown in Fig. 4 was determined. In accordance with this figure, a maximum emission intensity was obtained with a phosphor particle size in the vicinity of 6 μm, however just as in the case of $MgWO_4$, with particle sizes of 2 μm or less or 13 μm or more it was reduced to less than 20%. Accordingly, a phosphor particle size of 2 - 13 μm is preferred when using $CaWO_4$ phosphor.

Third embodiment

A solid-state light emitting element using Zn_2SiO_4 : Mn phosphor was obtained by the same method as in the first embodiment by applying this particulate phosphor layer on the substrate side walls including the pn junction portion so as to form the phosphor layer.

When a forward-biased current of 2.5 mA having a voltage of 25 V was applied between the electrodes of the solid-state light emitting element obtained in this way, a light emission spectrum having a peak wavelength at 525 nm was obtained which exhibited a green light emission.

Furthermore the relationship between relative emission intensity and phosphor particle size as shown in Fig. 6 was determined by varying the phosphor particle sizes. In accordance with this figure, a maximum emission intensity was obtained with a phosphor particle size in the vicinity of 5 μm, however when the particle size became 1.3 μm or less or 13 μm or more, the relative emission intensity was reduced to less than

20%, and there was no contribution to light emission. Accordingly, a phosphor particle size of 1.3 - 13 μm is preferred when using such a phosphor.

Fourth embodiment

A solid-state light emitting element using Y_2O_3 : Eu phosphor was obtained by the same method as in the first embodiment by applying this particulate phosphor layer on the substrate side walls including the pn junction portion so as to form the phosphor layer.

When a forward-biased current of 3.0 mA having a voltage of 30 V was applied between the electrodes of the solid-state light emitting element obtained in this way, a light emission spectrum having a peak wavelength at 611 nm was obtained which exhibited a green light emission.

Furthermore the relationship between relative emission intensity and phosphor particle size as shown in Fig. 7 was determined by varying the phosphor particle sizes. In accordance with this figure, a maximum emission intensity was obtained with a phosphor particle size in the vicinity of 4.2 μm, however when the particle size became 0.7 μm or less or 11 μm or more, the relative emission intensity was reduced to less than 20%, and there was no contribution to light emission. Accordingly, a phosphor particle size of 0.7 - 11 μm is preferred when using such a phosphor.

Fifth embodiment

A self-activating phosphor $MgWO_4$ was placed in a vacuum bell jar and a vacuum of about 1×10^{-6} - 6×10^{-6} mm Hg was adjusted. Under this condition, Ar gas was introduced, and MgWO[?] powder was sputtered in Ar atmosphere of 2 [?] 10 [?] - 2 [?] 10 [?] mm Hg; in the same way, a phosphor layer having a desired thickness was formed by the sputtering method by sputtering the $MgWO_4$ powder in the vacuum bell jar on the pn junction portion located on the opposite side, whereby a solid-state light emitting element was obtained.

When a forward-biased current of 2 mA having a voltage of 20 V was applied between the electrodes of the solid-state light emitting element obtained in this way, a light emission spectrum having a peak wavelength at 480 nm was obtained which exhibited a blue light emission. Furthermore $MgWO_4$ thin-film phosphor layers of various film thicknesses were respectively formed on the pn junction portions by the same method as set forth above, the light emission spectrum was measured, the relative

emission intensities at the peak wavelength of 480 nm were determined, and the relationship between relative emission intensity and phosphor particle size[sic!] as shown in Fig. 8 was determined. In accordance with this figure, when the phosphor particle size was 0.6 μm or less, the luminous efficiency of the phosphor was extremely poor and was reduced to less than 20% in comparison with a phosphor particle size of about 1 μm at which a maximum emission intensity was obtained, and there was hardly any contribution to light emission. With phosphor particle sizes of 2.6 μm and more, on the other hand, the relative emission intensity was equally reduced to less than 20%, so that the contribution to light emission was small. In accordance with the above, a particle size of 0.6 - 2.6 μm is preferred for the $MgWO_4$ making up the phosphor layer.

Sixth embodiment

A solid-state light emitting element was obtained with a self-activating phosphor $CaWO_4$ as a the test powder in the same way as in the fifth embodiment, by forming a phosphor layer by applying the $GaWO_4$[sic!] phosphor particles on the substrate side walls including the above mentioned pn junction portion by the vacuum sputtering method.

When a forward-biased current of 3.0 mA having a voltage of 30 V was applied between the electrodes of the solid-state light emitting element obtained in this way, a light emission spectrum having a peak wavelength at about 415 nm was obtained which exhibited a blue light emission.

Moreover CaWO[?] powder phosphor layers of various film thicknesses were respectively formed on the pn junction portion by the same method as set forth above, the light emission spectrum was measured, the relative emission intensities at the peak wavelength were determined, and the relationship between relative emission intensity and phosphor particle size[sic!] as shown in Fig. 9 was determined. In accordance with this figure, a maximum emission intensity was obtained in the vicinity of a phosphor grain film thickness of 1.6 μm, however just as in the case of $MgWO_4$, with film thicknesses of 0.6 μm or less or 2.6 μm or more it was reduced to less than 20%. Accordingly, a phosphor particle size of 0.6 - 2.6 μm is preferred when using $CaWO_4$ phosphor.

Seventh embodiment

A solid-state light emitting element using Zn_2SiO_4 : Mn phosphor was obtained by the same method as in the fifth embodiment by applying this particulate phosphor

layer on the substrate side walls including the pn junction portion os as to form the phosphor layer.

When a forward-biased current of 2.5 mA having a voltage of 25 V was applied between the electrodes of the solid-state light emitting element obtained in this way, a light emission spectrum having a peak wavelength at 525 nm was obtained which exhibited a green light emission.

Furthermore the relationship between relative emission intensity and phosphor particle size[sic!] as shown in Fig. 11 was moreover determined by varying the film thickness of the phosphor layer. In accordance with this figure, a maximum emission intensity was obtained in the vicinity of a phosphor layer film thickness of 1.4 μm, however when this film thickness became 0.4 μm or less or or 3.0 μm or more, the relative emission intensity was reduced to less than 20%, and there was no contribution to light emission. Accordingly, a particle size of 0.4 - 3.0 μm is preferred when using such a phosphor.

Eighth embodiment

A solid-state light emitting element using Y_2O_3 : Eu was obtained by the same method as in the fifth embodiment by applying this particulate phosphor layer on the substrate side walls including the pn junction portion so as to form the phosphor layer.

When a forward-biased current of 3.0 mA having a voltage of 30 V was applied between the electrodes of the solid-state light emitting element obtained in this way, a light emission spectrum having a peak wavelength at 611 nm was obtained which exhibited a green light emission.

Furthermore the relationship between relative emission intensity and phosphor particle size as shown in Fig. 11 was determined by varying the film thickness of the phosphor layer. In accordance with this figure, a maximum emission intensity was obtained at about 1 μm, however when this film thickness became 0.3 μm or less or 3.0 μm or more, the relative emission intensity was reduced to less than 20%, and there was no contribution to light emission. Accordingly, a phosphor particle size of 0.3 - 3.0 μm is preferred when using such a phosphor.

Effect of the invention

In accordance with the invention as set forth above, it is possible to furnish a highly reliable solid-state light emitting element providing various colors of emitted light while having the same kind of pn junction.

4. Short Explanation of the Drawings

Fig. 1 is a sectional view of a solid-state light emitting element being an embodiment of the present invention,

Fig. 2 is a sectional view of a solid-state light emitting element of the prior art,

Fig. 3 is a diagram showing the characteristic line for the emission spectrum of light radiation from the pn junction interface of a solid-state light emitting element of the present invention,

Fig. 4 - Fig. 7 are characteristic diagrams showing the relation between relative emission intensity and phosphor particle size in respective powder-type phosphors of different particle sizes,

Fig. 8 - Fig. 11 are characteristic diagrams showing the relation between relative emission intensity and phosphor film thickness in respective thin-film phosphors of different film thicknesses.

11 ..... p-type boron nitride crystal layer,
12 ..... np-type boron nitride crystal layers
13 ..... phosphor layer
14, 15 .... electrodes

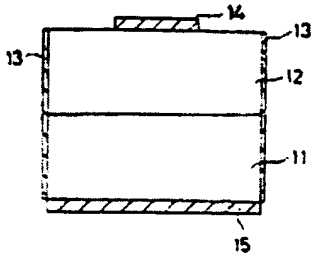

FIG. 1

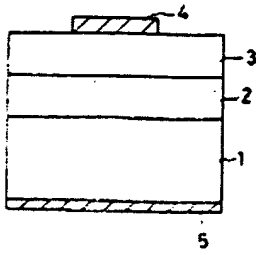

FIG. 2

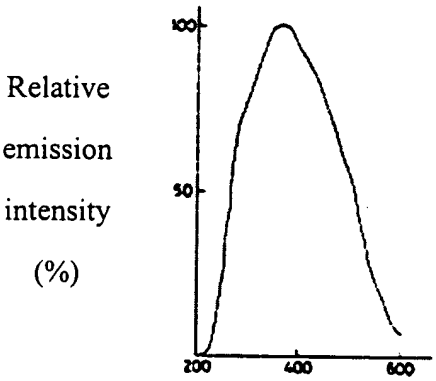

FIG. 3

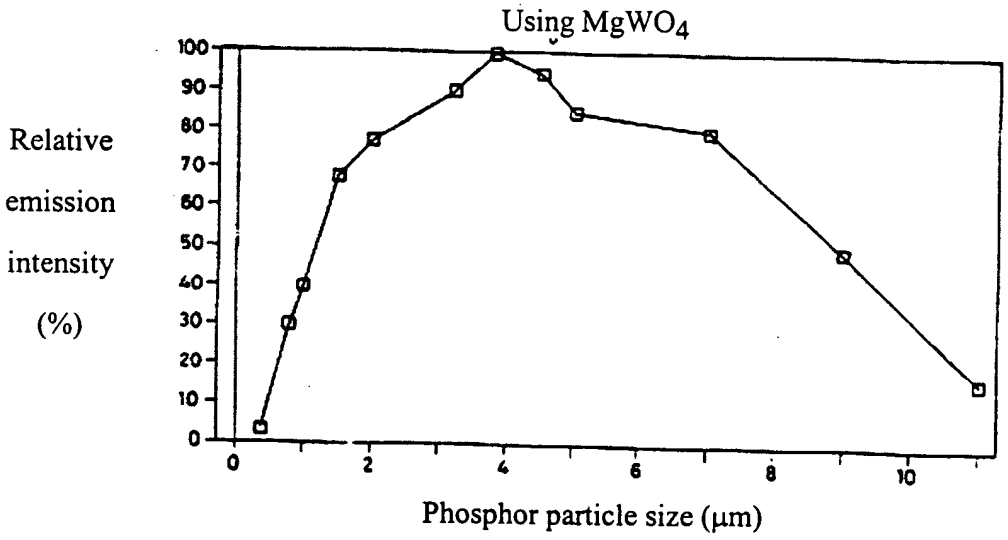

FIG. 4

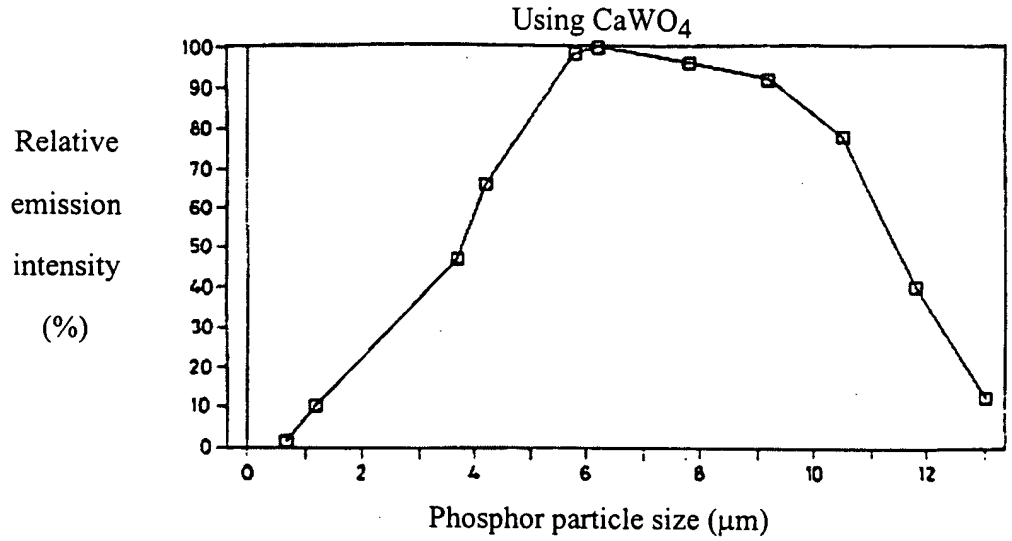
Using $CaWO_4$
Relative emission intensity (%)
100
90
80
70
60
50
40
30
20
10
0
0
2
4
6
8
10
12
Phosphor particle size (μm)

FIG. 5

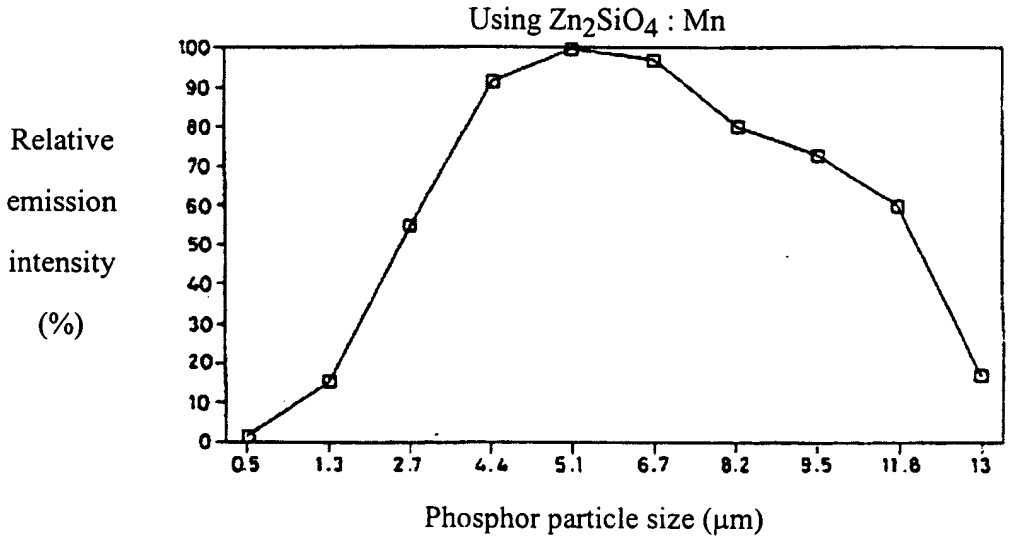
Using Zn_2SiO_4 : Mn
Relative emission intensity (%)
100
90
80
70
60
50
40
30
20
10
0
0.5
1.3
2.7
4.4
5.1
6.7
8.2
9.5
11.8
13
Phosphor particle size (μm)

FIG. 6

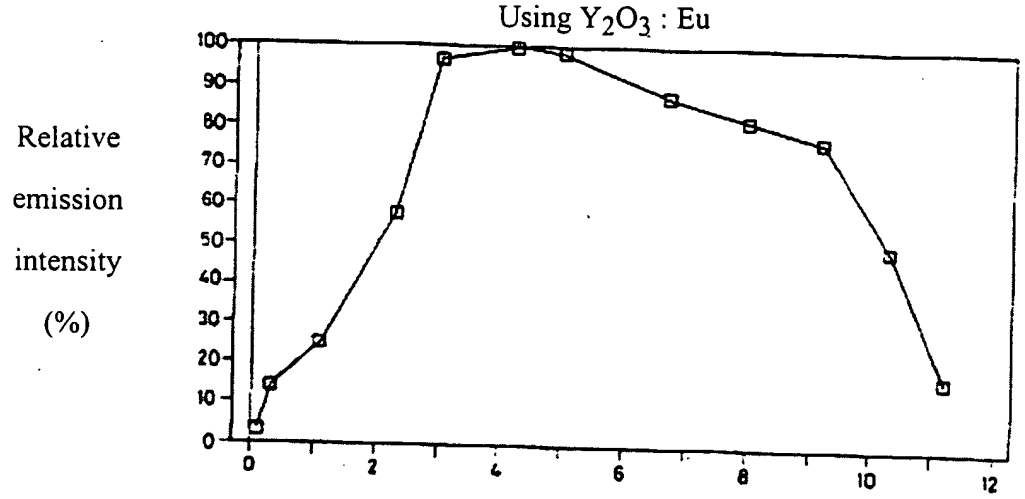
Using Y_2O_3 : Eu
Relative emission intensity (%)
100
90
80
70
60
50
40
30
20
10
0
0
2
4
6
8
10
12
Phosphor particle size (μm)

FIG. 7

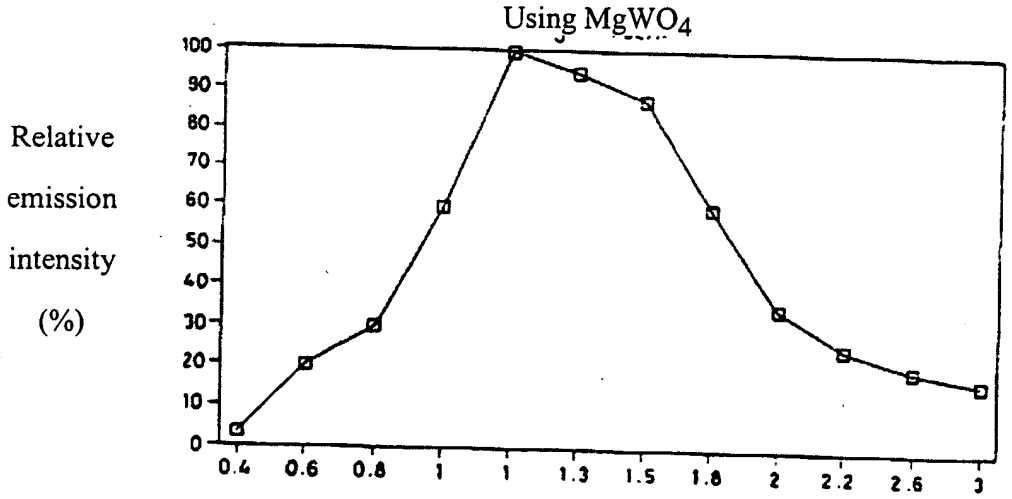
Using $MgWO_4$
Relative emission intensity (%)
100
90
80
70
60
50
40
30
20
10
0
0.4
0.6
0.8
1
1
1.3
1.5
1.8
2
2.2
2.6
3
Phosphor film thickness (μm)

FIG. 8

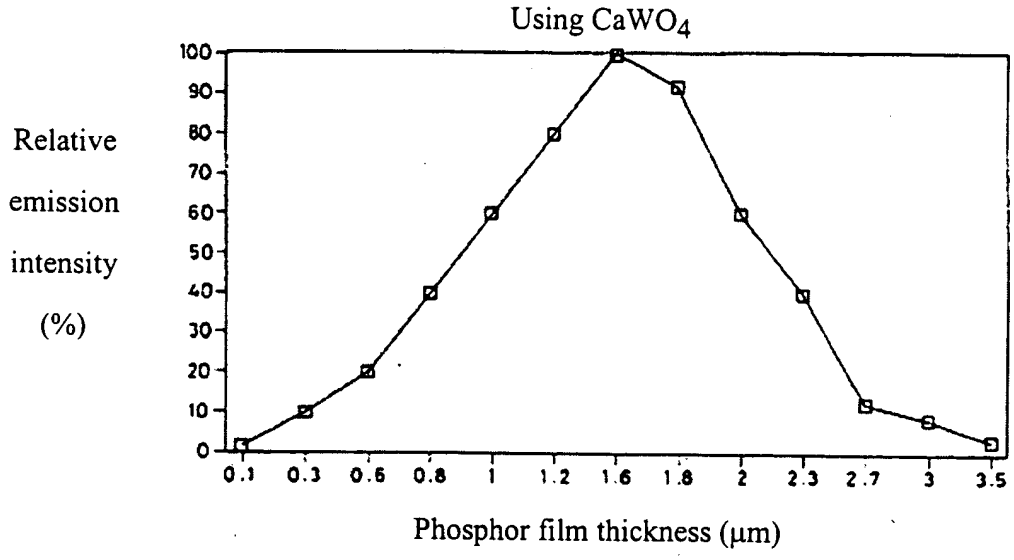
Using $CaWO_4$
Relative emission intensity (%)
100
90
80
70
60
50
40
30
20
10
0
0.1
0.3
0.6
0.8
1
1.2
1.6
1.8
2
2.3
2.7
3
3.5
Phosphor film thickness (μm)

FIG. 9

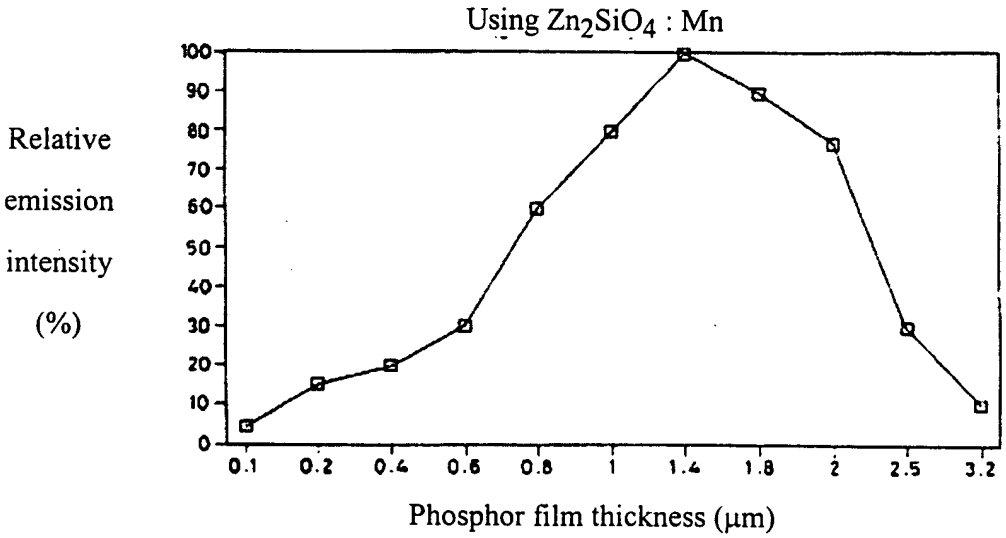
Using Zn_2SiO_4 : Mn
Relative emission intensity (%)
100
90
80
70
60
50
40
30
20
10
0
0.1
0.2
0.4
0.6
0.8
1
1.4
1.8
2
2.5
3.2
Phosphor film thickness (μm)

FIG. 10

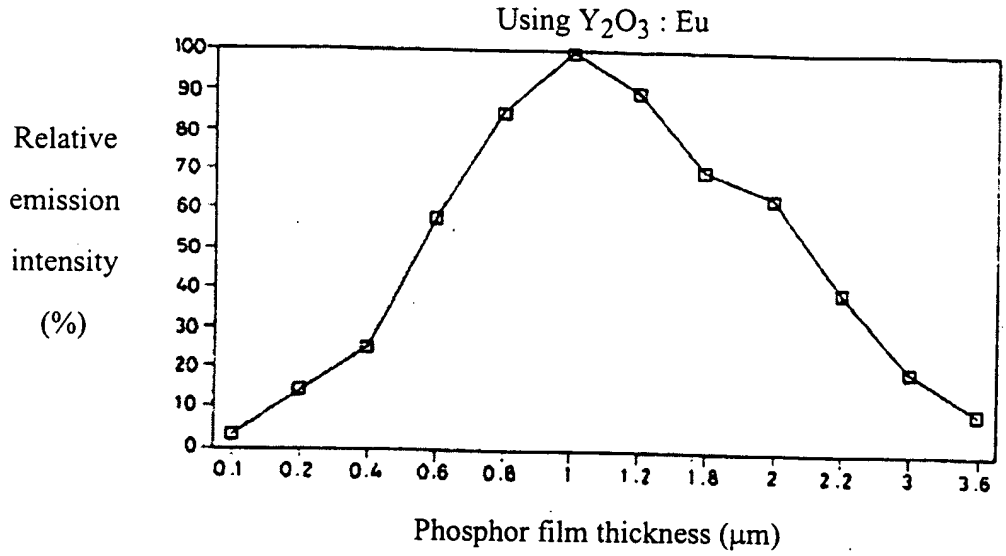
Using Y_2O_3 : Eu
Relative emission intensity (%)
100
90
80
70
60
50
40
30
20
10
0
0.1
0.2
0.4
0.6
0.8
1
1.2
1.8
2
2.2
3
3.6
Phosphor film thickness (μm)

FIG. 11

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⑫公開特許公報(A)　平2-91980

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C 30 B 29/38		8518-4G

⑬公開　平成2年(1990)3月30日

審査請求　未請求　請求項の数 2　(全9頁)

⑭発明の名称　固体発光素子

⑳特　願　昭63-244806
㉒出　願　昭63(1988)9月29日

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明細書

1．発明の名称

固体発光素子

2．特許請求の範囲

（1）微量なBeを含むP形窒化ホウ素結晶層及びこの結晶層上に形成された微量なSiを含むN形窒化ホウ素結晶層からなる基体と、少なくともこの基体の側部の前記P形、N形窒化ホウ素結晶層の接合面を覆う粒径0.3～13μmから構成された粒状の蛍光体層と、前記基体の上面、下面に夫々形成された電極とを具備することを特徴とする固体発光素子。

（2）微量なBeを含むP形窒化ホウ素結晶層及びこの結晶層上に形成された微量なSiを含むN形窒化ホウ素結晶層からなる基体と、少なくともこの基体の側部の前記P形、N形窒化ホウ素結晶層の接合面を覆う膜厚0.6～2.6μmの薄膜蛍光体層と、前記基体の上面、下面に夫々形成された電極とを具備することを特徴とする固体発光素子。

3．発明の詳細な説明

〔発明の目的〕

（産業上の利用分野）

本発明は、PN接合面を有する固体発行素子の改良に関する。

（従来の技術）

近年、エレクトロニクス技術の進展に伴い発光素子も放電管を用いたものばかりでなく、固体発光素子が広く用いられつつある。

従来、固体発光素子の代表的なものとしては、例えば第2図示す如く、N形GaP結晶基板1上にTeを微量含むN形GaPエピタキシャル層2及び微量のZn、Oを含むP形GaPエピタキシャル層3を形成させ、更にこのP形GaPエピタキシャル層3上及び前記基板1の裏面に夫々電極4、5を形成した構造の赤色発光素子が知られている。また、この他図示しないが、N型GaAs基板にGaAsP、GaAlAsのPN接合を利用した赤色発光素子、前記基板上におけるGaAs$_{1-x}$P$_x$のPN接合を利用した橙、黄色発光素

子、前記ＧａＰ上におけるＧａＰのＰＮ接合を利用した緑色発光素子、ＳｉＣ上のＳｉＣのＰＮ接合を利用した青色発光素子等が知られている。

しかし、これらの固体発光素子は、小型で電子回路との整合性が良いという利点の反面、夫々の種類の発光素子特有の発光波長に規制され、それ以外の発光色を選択しても、固体発光素子の種類自体も少なく、任意の発光色を得ることが困難であった。

（発明が解決しようとする課題）

本発明は上記事情に鑑みてなされたもので、様々な発光色をもちながらしかも同一種類のＰＮ接合を有する固体発光素子を提供することを目的とする。

〔発明の構成〕

（課題を解決するための手段）

本願第１の発明は、微量なＢｅを含むＰ形窒化ホウ素結晶層及びこの結晶層上に形成された微量なＳｉを含むＮ形窒化ホウ素結晶層からなる基体と、少なくともこの基体の側部の前記Ｐ形．Ｎ形窒化ホウ素結晶層の接合面を覆う粒径0.3 ～13μｍの粒から構成された粒状の蛍光体層と、前記基体の上面、下面に夫々形成された電極とを具備することを特徴とする固体発光素子である。

本願第２の発明は、微量なＢｅを含むＰ形窒化ホウ素結晶層及びこの結晶層上に形成された微量なＳｉを含むＮ形窒化ホウ素結晶層からなる基体と、少なくともこの基体の側部の前記Ｐ形．Ｎ形窒化ホウ素結晶層の接合面を覆う膜厚0.6 ～2.6μｍの薄膜蛍光体層と、前記基体の上面、下面に夫々形成された電極とを具備することを特徴とする固体発光素子である。

本願第１の発明において、粒状の蛍光体層を構成する粒径が0.3 ～13μｍの範囲を外れると、十分な発光強度が得られない。また、本願第２の発明においても、蛍光体層の膜厚が0.6 ～2.6 μｍの範囲を外れると、十分な発光強度が得られない。

本発明者等は、上記蛍光体層を形成する前、即ち順バイアス方向に例えば０．５ｍＡの電流を流した場合、第３図に示す如く、主に200 ～400nmの紫外域にピーク波長を有する発光スペクトルをを得た。そこで、本発明者等はＰＮ接合上に粒径や膜厚の異なる様々な蛍光体層を形成させて実験を試みたところ、上記に記載した発明を得るに至ったものである。

以下、本発明について第１図を参照して更に詳しく説明する。

図中の11は、微量なＢｅを含むＰ形窒化ホウ素結晶層（以下、Ｐ形層という）である。このＰ形層11上には、微量なＳｉを含むＮ形窒化ホウ素結晶層（以下、Ｎ形層という）12が形成されている。ここで、前記Ｐ形層11とＮ形層12を総称して基体と呼ぶ。この基体の側壁には、粒径0.3 ～13μｍの粒から構成された粒状の蛍光体層13が形成されている。なお、この蛍光体層13は、基体の側壁全体に亙って形成されている必要はなく、少なくともＰ形層11とＮ形層12の接合部分を覆っていればよい。前記基体の上面．下面には、夫々電極14．15が形成されている。

（作用）

本発明によれば、ＰＮ接合上に粒径や膜厚の異なる様々な蛍光体層を形成させることにより、様々な発光色をもちながらしかも同一種類のＰＮ接合を有する固体発光素子を得ることができる。

（実施例１）

自己付活蛍光体$MgWO_4$を、ニトロセルロース６wt%、エタノール2.5 wt%、ブチルアセテート86.5wt%、ジエチルフタレート5.0wt %からなる溶液に撹拌．混合した。次に、この$MgWO_4$粒子を前述したＰＮ接合部分を含む基体側壁に塗布し400 ℃に加熱後、室温に冷却して蛍光体層を形成し、固体発光素子を得た。

こうして得られた固体発光素子に順バイアス方向に電極間電圧20Ｖ、電流２ｍＡを流したところ、480nmにピーク波長が存在する発光スペクトルが得られ、青色発光を示した。また、粒径の異なる$MgWO_4$粉体蛍光体層をＰＮ接合部分に上記と同様な方法で夫々形成させて発光スペクトル

を測定し、480nmのピーク波長における相対発光強度を求め、第4図に示す相対発光強度と蛍光体粒径との関係を求めた。同図により、蛍光体粒径が0．6μm以下の場合、蛍光体の発光効率が極めて悪く、最大発光強度が得られる蛍光体粒径4．0μm前後の発光強度に比較して20%以下に低下し、ほとんど発光に対する寄与はなかった。一方、蛍光体粒径が11μm以上の場合も同様に相対発光強度は20%以下に低下し、発光に対する寄与は少なかった。以上より、蛍光体層を構成する$MgWO_4$の粒径は0．6～11μmが好ましい。

（実施例2）

自己付活蛍光体$CaWO_4$を試料粉末として実施例1と同様に、有機溶液中に分散、懸濁混合した。次に、この$CaWO_4$粒子を前述したPN接合部分を含む基体側壁に塗布し乾燥後470℃に加熱し、室温に冷却して蛍光体層を形成し、固体発光素子を得た。

こうして得られた固体発光素子に順バイアス方向に電極間電圧30V、電流3mAを流したところ、525nmにピーク波長を有する発光スペクトルが得られ、緑色発光を示した。

また、蛍光体粒径を変化させ、第6図に示す相対発光強度と蛍光体粒径との関係を求めた。同図により、蛍光体粒径が5μmの付近で最大の発光強度が得られたが、粒径が1．3μm以下または13μm以上になると、相対発光強度が20%以下に低下し、発光への寄与はなかった。従って、こうした蛍光体を使用した場合、蛍光体粒径は、1．3～13μmが好ましい。

（実施例4）

蛍光体Y_2O_3：Euを使用して実施例1と同様な方法でこの粒子からなる蛍光体層をPN接合部分を含む基体側壁に塗布して蛍光体層を形成し、固体発光素子を得た。

こうして得られた固体発光素子に順バイアス方向に電極間電圧30V、電流3．0mAを流したところ、611nmにピーク波長を有する発光スペクトルが得られ、緑色発光を示した。

また、蛍光体粒径を変化させ、第7図に示す相対発光強度と蛍光体粒径との関係を求めた。同図により、蛍光体粒径が4．2μmの付近で最大の発光強度が得られたが、粒径が0．7μm以下または11μm以上になると、相対発光強度が20%以下に低下し、発光への寄与はなかった。従って、こうした蛍光体を使用した場合、蛍光体粒径は、0．7～11μmが好ましい。

（実施例5）

自己付活蛍光体$MgWO_4$を真空ベルジャ内に入れ、真空度を1×10^{-6}～6×10^{-6}mm Hg程度にする。この状態でArガスを導入し、2 10～2 10 mm HgAr雰囲気中で$MgWO_4$粉末をスパッタ、同じく真空ベルジャ内の$MgWO_4$粉末と反対側に設置したPN接合部分に所望の厚みの蛍光体層をスパッタリング法により形成し、固体発光素子を得た。

こうして得られた固体発光素子に順バイアス方向に電極間電圧20V、電流2mAを流したところ、480nmにピーク波長が存在する発光スペクトルが得られ、青色発光を示した。また、膜厚の異

なるMgWO$_4$薄膜蛍光体層をPN接合部分に上記と同様な方法で夫々形成させて発光スペクトルを測定し、480nmのピーク波長における相対発光強度を求め、第8図に示す相対発光強度と蛍光体粒径との関係を求めた。同図により、蛍光体粒径が0.6μm以下の場合、蛍光体の発光効率が極めて悪く、最大発光強度が得られる蛍光体粒径1μm前後の発光強度に比較して20%以下に低下し、ほとんど発光に対する寄与はなかった。一方、蛍光体粒径が2.6μm以上の場合も同様に相対発光強度は20%以下に低下し、発光に対する寄与は少なかった。以上より、蛍光体層を構成するMgWO$_4$の粒径は0.6～2.6μmが好ましい。

（実施例6）

自己付活蛍光体CaWO$_4$を試料粉末として実施例5と同様に、真空スパッタリング法にてGaWO$_4$粒子を前述したPN接合部分を含む基体側壁に塗布して蛍光体層を形成し、固体発光素子を得た。

こうして得られた固体発光素子に順バイアス方向に電極間電圧25V、電流2.5mAを流したところ、525nmにピーク波長を有する発光スペクトルが得られ、緑色発光を示した。

また、蛍光体層の膜厚を変化させ、第10図に示す相対発光強度と蛍光体粒径との関係を求めた。同図により、蛍光体層の膜厚が1.4μmの付近で最大の発光強度が得られたが、膜厚が0.4μm以下または3.0μm以上になると、相対発光強度が20%以下に低下し、発光への寄与は少なかった。従って、こうした蛍光体を使用した場合、蛍光体粒径は、0.4～3.0μmが好ましい。

（実施例8）

蛍光体Y$_2$O$_3$：Euを使用して実施例5と同様な方法でこの粒子からなる蛍光体層をPN接合部分を含む基体側壁に塗布して蛍光体層を形成し、固体発光素子を得た。

こうして得られた固体発光素子に順バイアス方向に電極間電圧30V、電流3.0mAを流したところ、611nmにピーク波長を有する発光スペクトルが得られ、赤色発光を示した。

また、蛍光体層の膜厚を変化させ、第11図に示す相対発光強度と蛍光体粒径との関係を求めた。同図により、1μm前後で最大発光強度がえられたが、その膜厚がが0.3μm以下または3.0μm以上になると、相対発光強度が20%以下に低下し、発光への寄与はなかった。従って、こうした蛍光体を使用した場合、蛍光体粒径は、0.3～3.0μmが好ましい。

［発明の効果］

以上詳述した如く本発明によれば、様々な発光色をもちながらしかも同一種類のPN接合を有する信頼性の高い固体発光素子を提供できる。

4．図面の簡単な説明

第1図は本発明の一実施例に係る固体発光素子の断面図、第2図は従来の固体発光素子の断面図、第3図は本発明に係る固体発光素子のPN接合面からの放射光の発光スペクトル特性図、第4図～第7図は夫々異なる粒径の粉体蛍光体による

こうして得られた固体発光素子に順バイアス方向に電極間電圧30V、電流3mAを流したところ、415nm前後にピーク波長を持つ発光スペクトルが得られ、青色発光を示した。

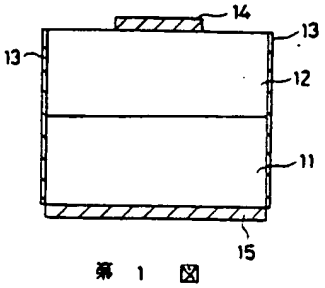
また、膜厚の異なるCaWO$_4$粉体蛍光体層をPN接合部分に上記と同様な方法で夫々形成させて発光スペクトルを測定し、ピーク波長における相対発光強度を求め、第9図に示す相対発光強度と蛍光体粒径との関係を求めた。同図により、蛍光体粒膜厚が1.6μm付近で最大の発光強度が得られたが、MgWO$_4$の場合と同様、膜厚が0.6μm以下または2.6μm以上になると、20%以下に低下した。従って、CaWO$_4$蛍光体を使用した場合、蛍光体粒径は、0.6～2.6μmが好ましい。

（実施例7）

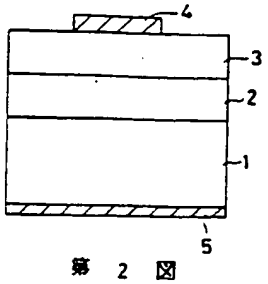
蛍光体Zn$_2$SiO$_4$：Mnを使用して実施例5と同様な方法でこの粒子からなる蛍光体層をPN接合部分を含む基体側壁に塗布して蛍光体層を形成し、固体発光素子を得た。

相対発光強度と発光体粒径との関係を示す特性図、第8図～第11図は夫々異なる膜厚の薄膜蛍光体~~粒子~~による相対発光強度と発光体膜厚との関係を示す特性図である。

11－P形窒化ホウ素結晶層、12－NP形窒化ホウ素結晶層、13－蛍光体層、14、15－電極。

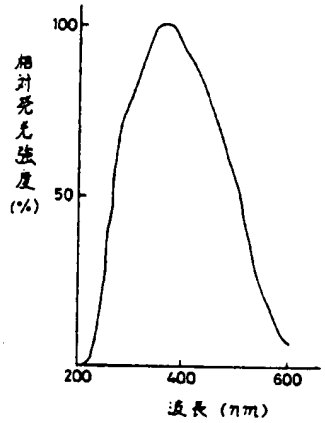


第 1 図

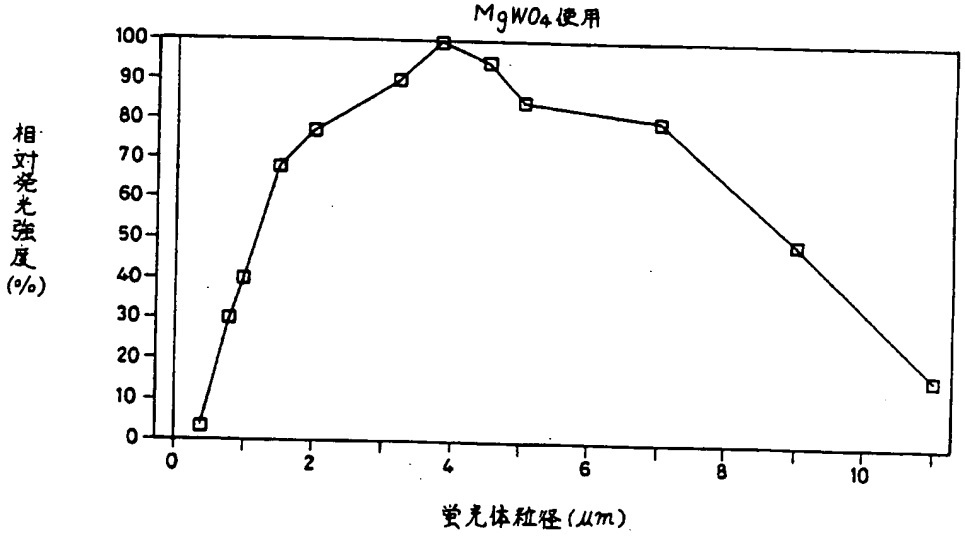


第 2 図

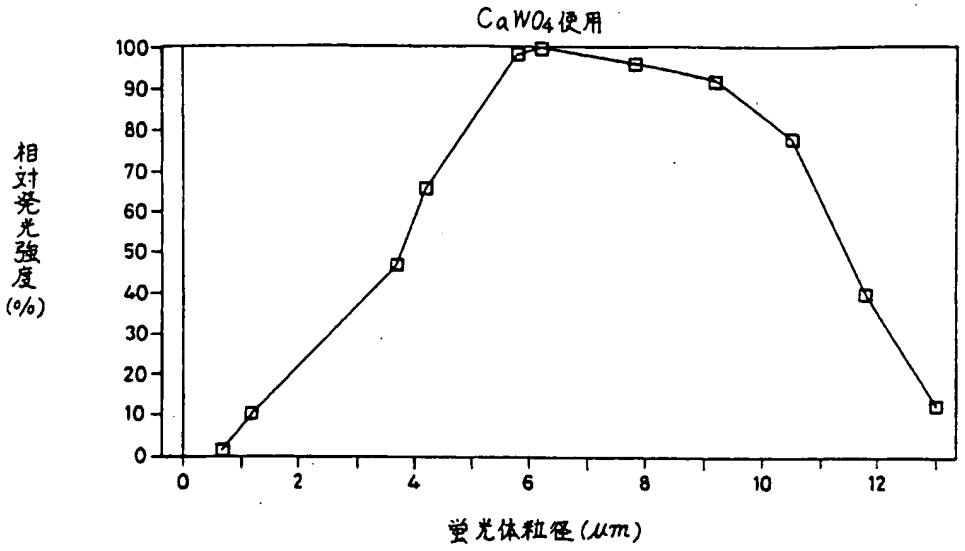
出願人代理人　弁理士　鈴江武彦



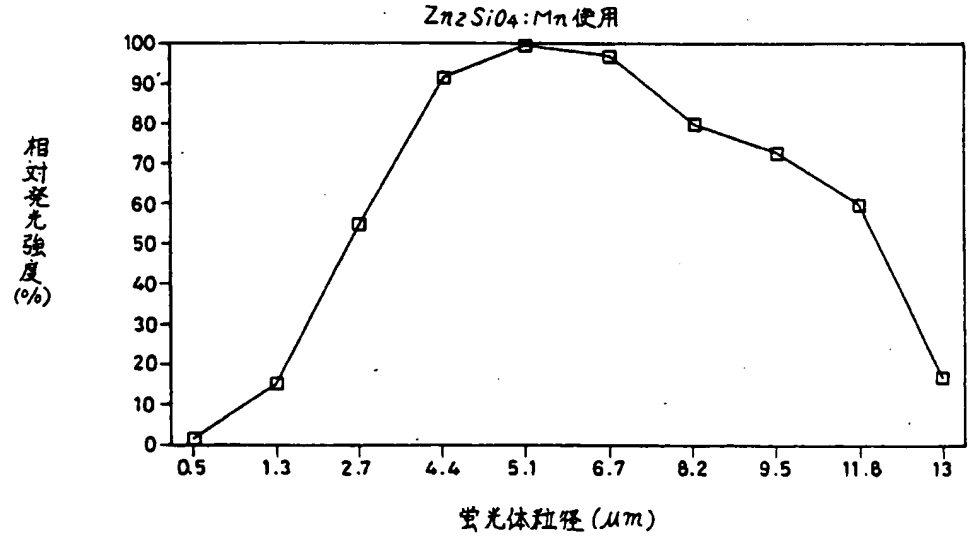
第 3 図



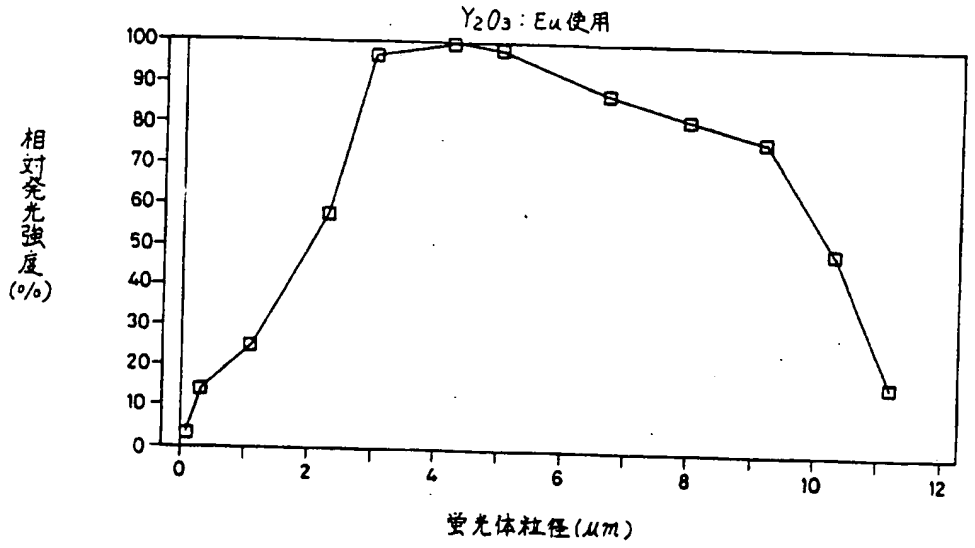
第 4 図


CaWO4使用
相対発光強度(%)
100
90
80
70
60
50
40
30
20
10
0
0
2
4
6
8
10
12
蛍光体粒径(μm)

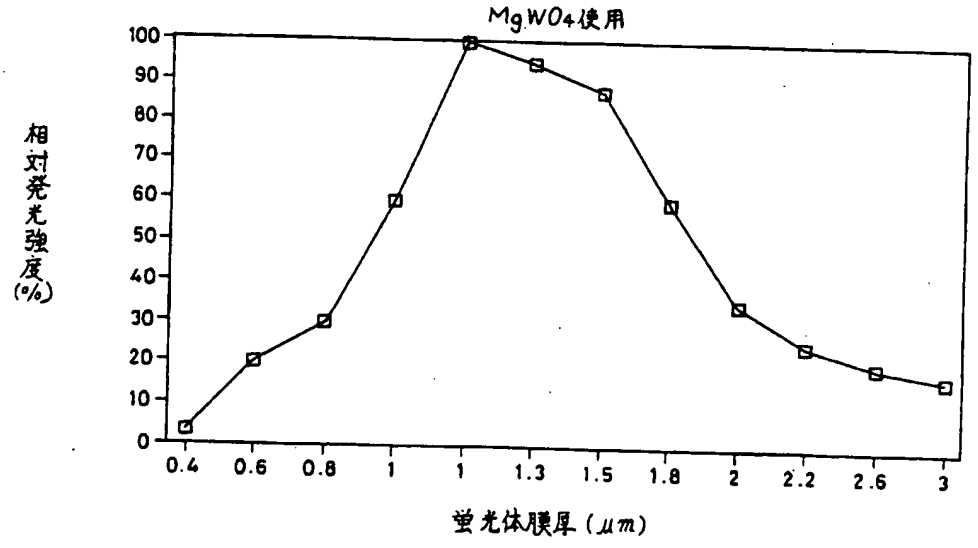
第 5 図


Zn2SiO4:Mn使用
相対発光強度(%)
100
90
80
70
60
50
40
30
20
10
0
0.5
1.3
2.7
4.4
5.1
6.7
8.2
9.5
11.8
13
蛍光体粒径(μm)

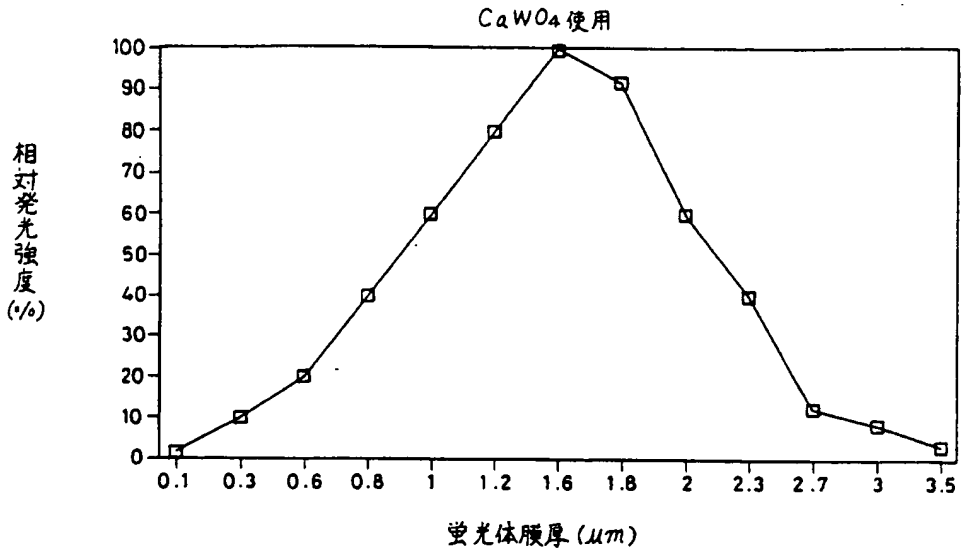
第 6 図


Y_2O_3：Eu使用
相対発光強度(%)
100
90
80
70
60
50
40
30
20
10
0
0
2
4
6
8
10
12
蛍光体粒径(μm)

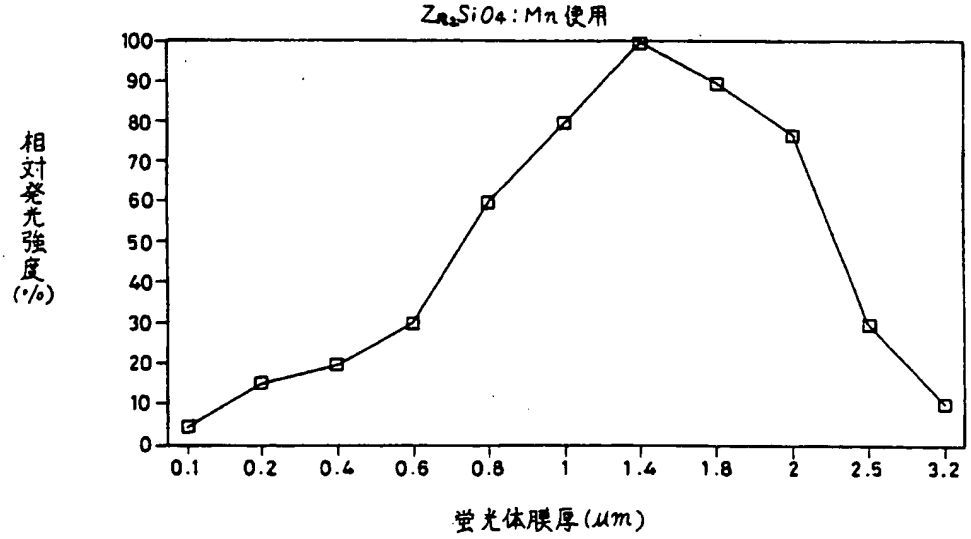
第 7 図


$MgWO_4$使用
相対発光強度(%)
100
90
80
70
60
50
40
30
20
10
0
0.4
0.6
0.8
1
1
1.3
1.5
1.8
2
2.2
2.6
3
蛍光体膜厚(μm)

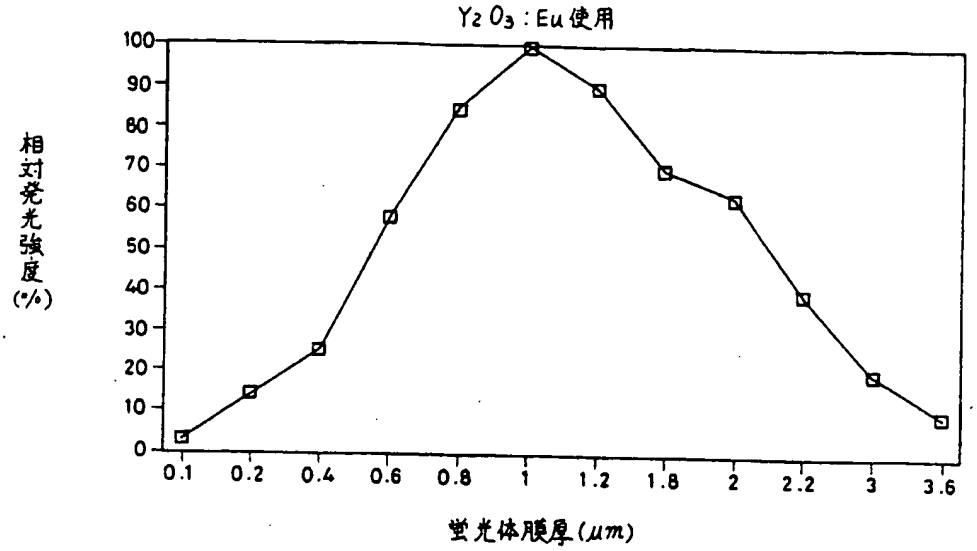
第 8 図


CaWO4使用
相対発光強度(%)
100
90
80
70
60
50
40
30
20
10
0
0.1
0.3
0.6
0.8
1
1.2
1.6
1.8
2
2.3
2.7
3
3.5
蛍光体膜厚(μm)

第 9 図


Zn2SiO4:Mn使用
相対発光強度(%)
100
90
80
70
60
50
40
30
20
10
0
0.1
0.2
0.4
0.6
0.8
1
1.4
1.8
2
2.5
3.2
蛍光体膜厚(μm)

第 10 図


Y2O3:Eu使用
相対発光強度(%)
100
90
80
70
60
50
40
30
20
10
0
0.1
0.2
0.4
0.6
0.8
1
1.2
1.8
2
2.2
3
3.6
蛍光体膜厚(μm)

第 11 図